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Ionic Liquid Crystals Based on Pyridinium Salts

Viorel Cîrcu

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/65757>

Abstract

This chapter describes the liquid crystalline properties of the ionic liquid crystals (ILC) based on pyridinium salts as well as their metal-containing compounds with an emphasis on the recent systems described in literature. The main factors that influence the liquid crystalline properties of pyridinium ILC are discussed. Selected thermal data are given according to mesogenic group employed and its position (either N-substitution or pyridinium ring substitution) and the number of structural cationic units (mono-, di-, or polycationic pyridinium ILC).

Keywords: ionic liquids, liquid crystals, pyridinium salts

1. Introduction

Ionic liquid crystals (ILCs) are extensively studied nowadays due to their unique properties resulting from the combination of liquid crystal (LC) and ionic liquid (IL) properties. Several reviews covering this topic were published in the recent years [1–3]. The field of ILCs is continuously growing as many recent applications were found: solar cells, membranes, battery materials, electrochemical sensors, or electroluminescent switches. Different factors are responsible for governing the nature of ILC phases, such as the molecular shape, location, and size of ionic groups, intermolecular interactions, and microphase segregation. Thus, the hydrophobic interactions between the long alkyl chain groups, ionic, dipole-dipole, anion–cation hydrogen bonding, and cation- π interactions together with the π - π stacking of the aromatic rings, all have a contribution to the stabilization of the liquid crystalline phase. For instance, there is a strong tendency to stabilize lamellar (smectic) phases, with SmA the most common phase for ILC, due to electrostatic interactions and ion-ion stacking in ILC. The combination of all these factors leads to LC behavior ranges from typical calamitic materials to discotic. The imidazolium or pyridinium derivatives, one of the most studied classes of ILC, with weakly coordinating anions, such as tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-), are well known for their high thermal and electrochemical stabilities. It is worth to

mention here that the pyridinium-based ILC has been known for a long time, displaying very similar properties with the related imidazolium-based ILC.

The most common types of LC phases displayed by ILCs are represented in **Figure 1**. Their identification relies upon three characterization techniques: polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffraction (XRD). The usual textures seen by POM for different mesophases are presented in **Figure 2**. It is very common to see the SmA phase of ionic mesogens as a so-called oily streak texture by POM, in particular during heating runs (**Figure 2**). When cooling from the isotropic state, very often the SmA phase can develop spontaneous homeotropic alignment due to interactions developed between the cationic groups and the glass substrate surface (the samples are sandwiched between two microscope slides), and further orientation of the mesogenic groups. As a result, the microscopy image contains large dark regions corresponding to these homeotropic alignments.

The POM technique is an important tool for mesophase identification, but an ultimate technique that confirms unequivocally the phase type is the XRD method. The latter one can give also important information regarding the internal organization within the mesophase resulting from the different molecular packing related to the chemical structure of the ionic mesogens and the nature of interactions between them.

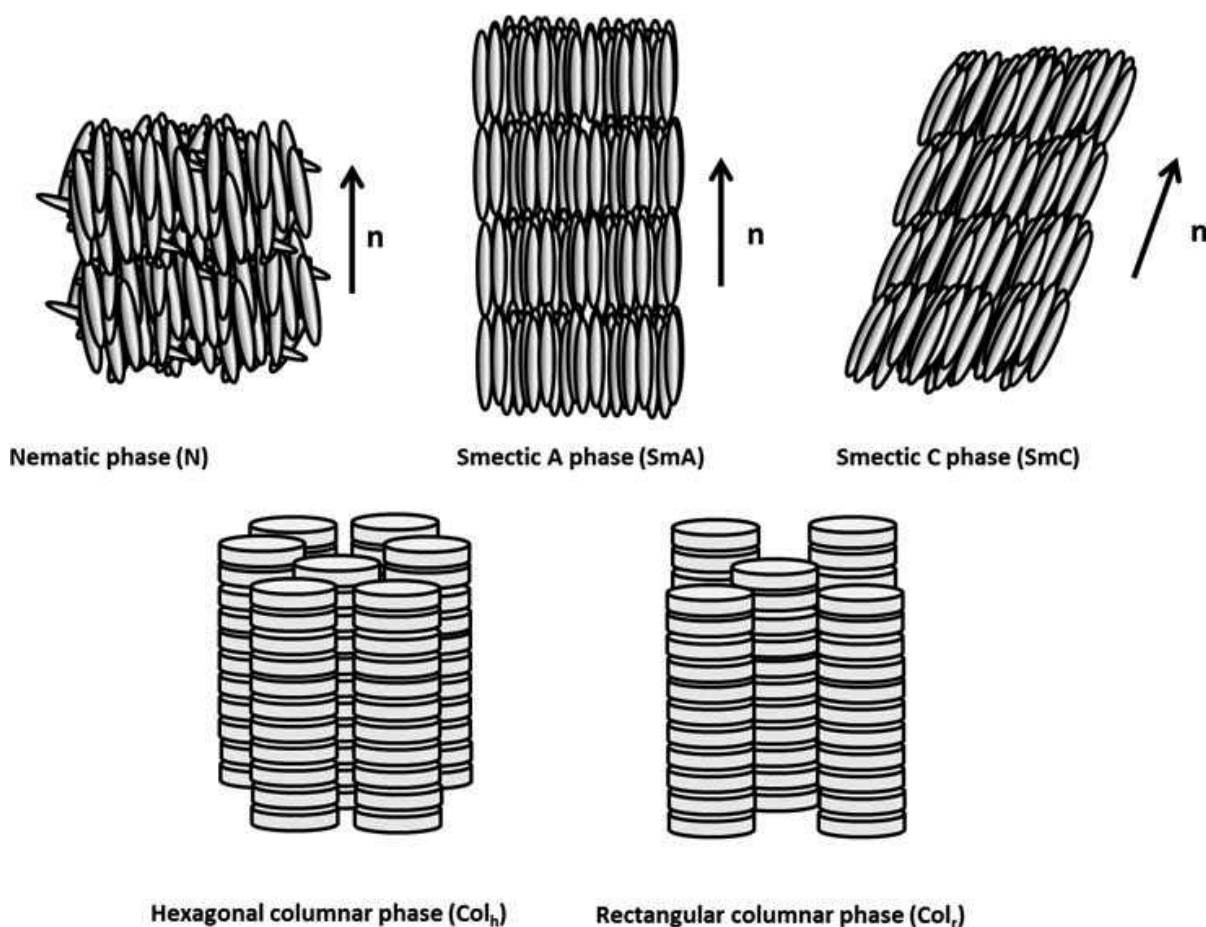


Figure 1. Schematic representation of the most common liquid crystalline phases encountered for ionic liquid crystals.

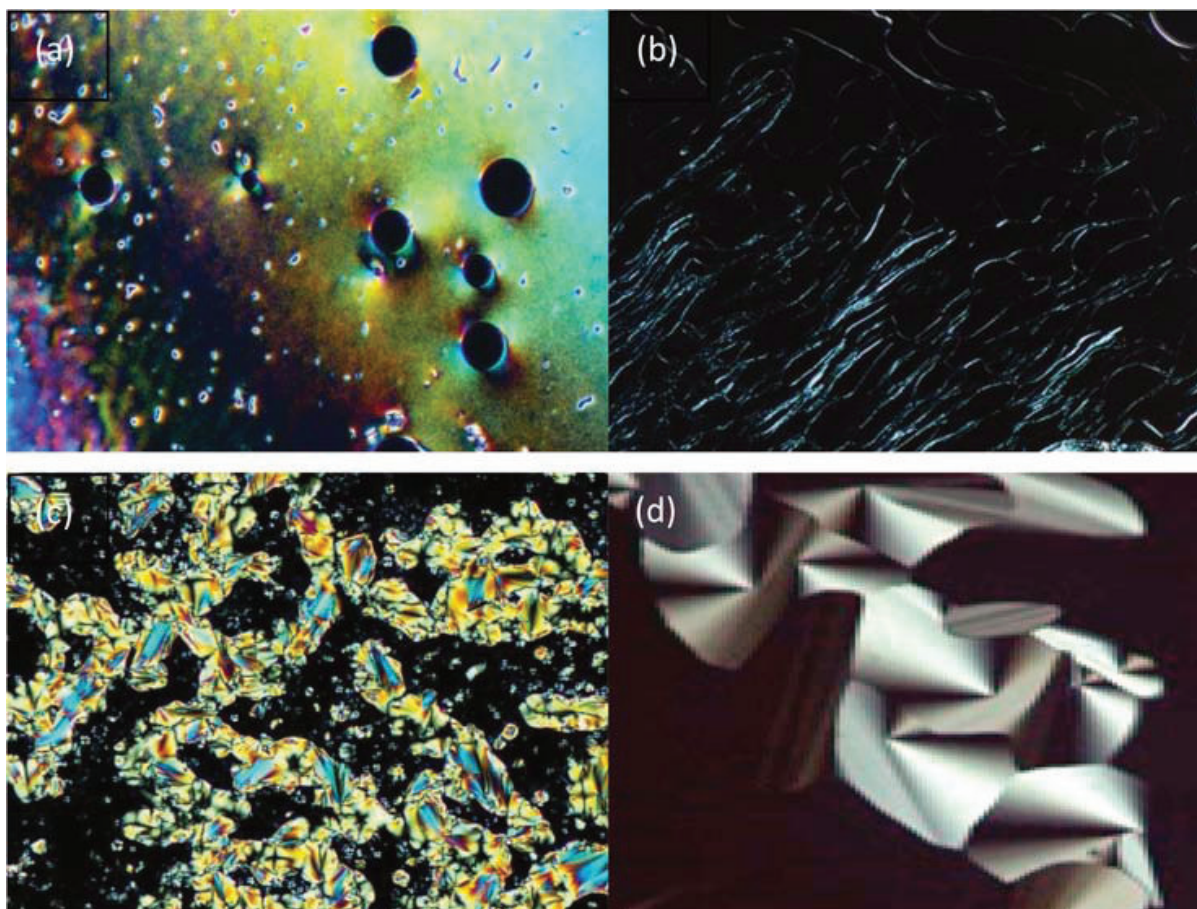


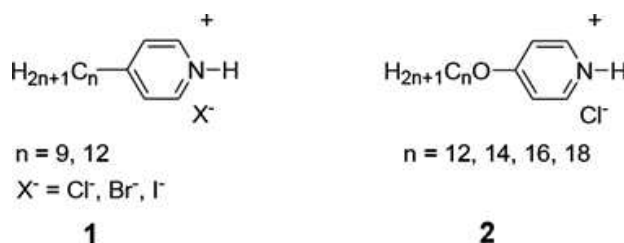
Figure 2. Typical textures for LC phases: marbled texture of a nematic phase (a), oily-streaks texture for a SmA phase on heating run (b), focal conical fan-shaped texture for SmA phase (c), and fan-shaped texture of a hexagonal columnar phase Col_h (d).

The thermal behavior as well as the mesophase type of pyridinium-based ILCs depends on several factors: the position and the nature of the mesogenic group attached to the pyridinium ring and the counterion employed. These structural factors will be discussed further and selected examples will be presented to illustrate their influence on the mesomorphic behavior. The pyridinium-based ILC classification was made according to mesogenic group used and its position (either N-substitution or pyridinium ring substitution) and the number of cationic units contained in their structure (mono-, di-, or polycationic pyridinium ILC).

2. Monocationic pyridinium ionic liquid crystals

2.1. Simple protonated pyridinium salts

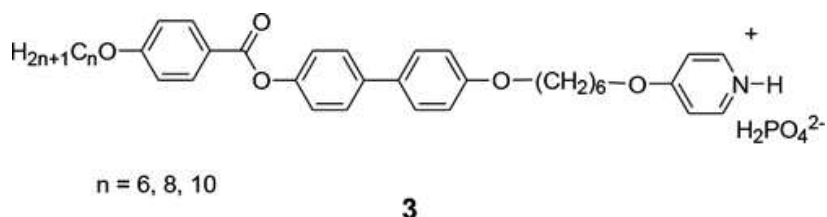
The simplest 4-alkyl substitution protonated pyridinium salts with halide as counterions (**1**) show no liquid crystalline properties as they melt straight to the isotropic phase. Such products have been synthesized by reaction between the corresponding hydrogen halide with their corresponding 4-alkyl pyridine compounds [4].



2a, $n = 12$ Cr 92 Cr' 122 SmA 133 dec
2b, $n = 14$ Cr 95 Cr' 122 SmA 139 dec
2c, $n = 16$ Cr 95 Cr' 124 SmA 142 dec
2d, $n = 18$ Cr 93 Cr' 124 SmA 145 dec

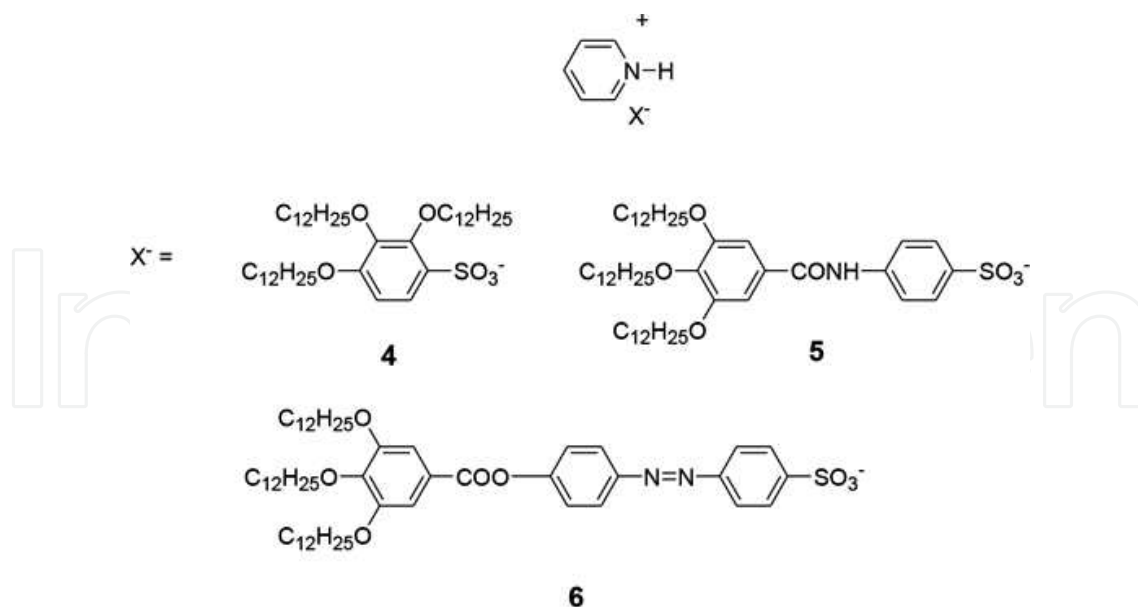
By changing the alkyl group with an alkoxy group, the resulting protonated chloride pyridinium salts show a SmA phase, with decomposition near the isotropization process. The melting and isotropization temperatures of these products were very insensitive to the chain lengths, suggesting that the hydrophobic interactions are the least significant factor in the thermal behavior of such protonated pyridinium salts [5].

A series of more elaborated protonated pyridinium salts have been prepared by the reaction between pyridine derivatives and phosphoric acid with the aim of studying their anhydrous proton conduction. X-ray diffraction measurements suggested that the pyridinium salts formed a bilayer structure with head-to-head configuration in the SmA phase [6].

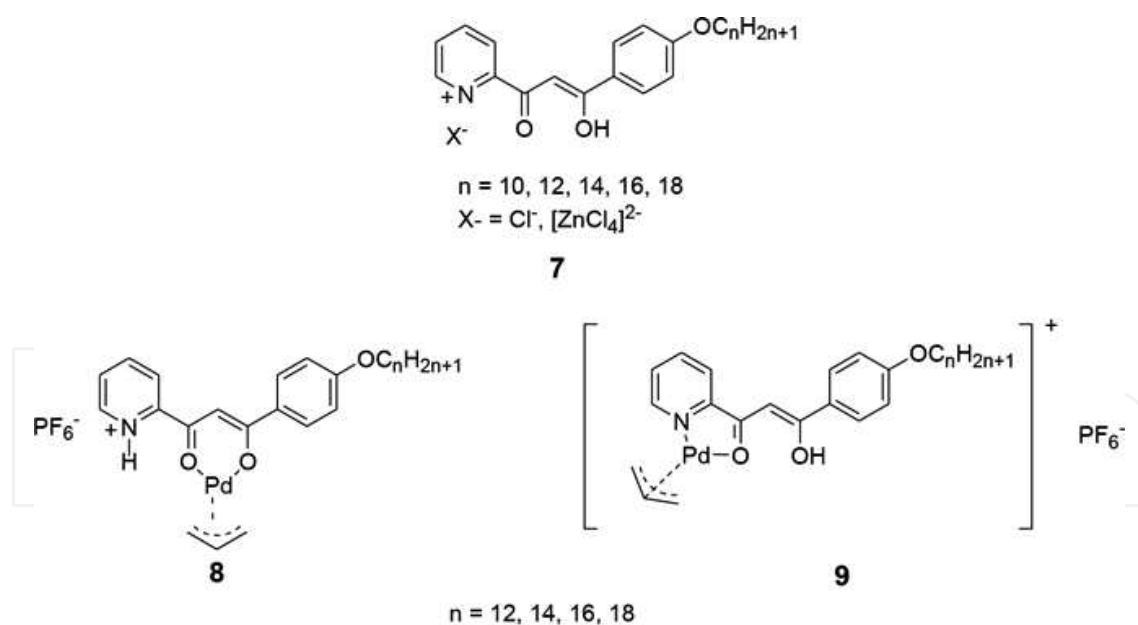


3a, $n = 6$; Cr 170 SmA 235 dec
3b, $n = 8$; Cr 169 SmA 232 dec
3c, $n = 10$; Cr 159 SmA 213 dec

The protonated pyridinium cation was employed to generate liquid crystalline materials having as counterions a series of wedge-shaped benzenesulfonate mesogens **4–6** [7, 8]. Compound **4**, having a rather unusual substitution pattern, 2,3,4-tris(dodecyloxy)benzenesulfonate, exhibits a reversible transition from a columnar disordered phase into an ordered columnar during the slow heating and cooling cycles. The thermal behavior of pyridinium salts **5** and **6** was compared to thermal properties of their corresponding benzenesulfonic acid and its sodium salts. It was found that **5** and **6** exhibit much lower transition temperatures than the sulfonic acids (the corresponding sulfonic acid of **6** was not stable upon drying) and sodium salts, respectively.



4, Cr 30 Cr' 53 Cr" 80 Col_{hd} 122 Iso
5, Cr 39 M 65 Iso
6, Cr 94 Col 200 Iso (dec)



8, $n = 14$, Cr 84 Cr' 158 SmC 170 Iso **9**, $n = 14$, Cr 76 SmC 173 Iso

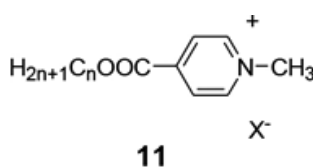
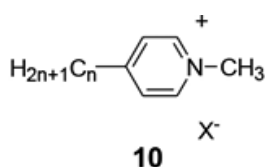
When the protonated pyridinium moiety is part of a α -diketone compound, the resulting β -diketone pyridinium chloride salts are not mesomorphic. Replacement of chloride anion with the tetrachlorozincate ion produced mesomorphic ionic salts displaying a SmA phases over a

broad temperature range [9]. The same authors reported the thermal behavior and photophysical properties of the metal-free β -diketone pyridinium ligands, and their allyl-palladium(II) complexes (**8**, **9**) [10, 11]. Interestingly, an equilibrium between **8** and **9** exists in solution. Another peculiar aspect about these complexes is that normally, the β -diketone ligands are first deprotonated before coordination to the metal center. Pd(II) metallomesogens with tetradecyloxy groups display a SmC phase, with reduced mesomorphic range for the protonated compound. The emission properties of Pd(II) complexes were preserved in the LC state.

2.2. N-alkylated pyridinium salts

2.2.1. N-methyl pyridinium salts

A clear trend for isotropization temperatures was seen for N-methyl pyridinium salts, meaning that, based on strong dependence of these temperatures on the alkyl chain length, longer alkyl chain length in position 4 of the pyridinium ring lead to higher transition temperatures. Moreover, it was observed that the 1-methyl-4-alkoxycarbonylpyridinium iodides salts have thermochromic properties. Color changes were observed on heating at both crystal to crystal and crystal to mesophase transitions, while such an observation could not be made for the 1-methyl-4-alkylpyridinium iodides salts [4, 12, 13].



10a, $n = 8$, $X^- = I^-$: Cr 103 Iso

10b, $n = 10$, $X^- = I^-$: Cr 113 Iso

10c, $n = 11$, $X^- = I^-$: Cr 116 SmA Iso

10d, $n = 12$, $X^- = I^-$: Cr 113 SmA 153 Iso

10e, $n = 12$, $X^- = ClO_4^-$: Cr 93 SmA 95 Iso

10f, $n = 13$, $X^- = I^-$: Cr 112 SmA 188 Iso

10g, $n = 14$, $X^- = I^-$: Cr 116 SmA 209 Iso

11a, $n = 10$, $X^- = I^-$: Cr 86 SmA154 Iso

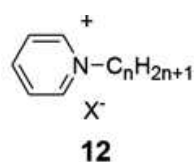
11b, $n = 12$, $X^- = I^-$: Cr 94 SmA 178 Iso

11c, $n = 14$, $X^- = I^-$: Cr 99 SmA 182 Iso

11d, $n = 16$, $X^- = I^-$: Cr 103 SmA 182 Iso

2.2.2. Other N-alkylated pyridinium salts

The simple N-alkylated chloride pyridinium salts **12** were obtained by reacting the corresponding alkyl chloride and pyridine, while the tetrachlorometalates, where $M = Co(II)$ or $Ni(II)$, were prepared by the reaction between these chloride pyridinium salts and anhydrous metallic chlorides [14]. The N-alkylated pyridinium chloride salts with a chain length below 12 units do not display liquid-crystal behavior.

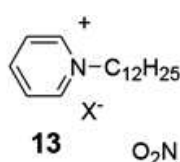


$X^- = \text{Cl}^-$, $[\text{MCl}_4]^{2-}$ (where $\text{M} = \text{Co}, \text{Ni}$)
 $n = 12, 14, 16, 18$

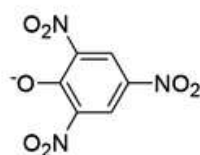
$X^- = \text{PF}_6^-$
 $n = 12, 14, 16, 18$

$X^- = \text{C}_m\text{H}_{2m+1}\text{OSO}_3^-$
 $m = 10, 12, 14, 16, 18, 20$
 $n = 6, 8, 10, 12, 14, 16, 18, 20$

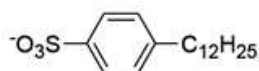
$X^- = [\text{CuCl}_4]^{2-}$
 $n = 6, 9-18$



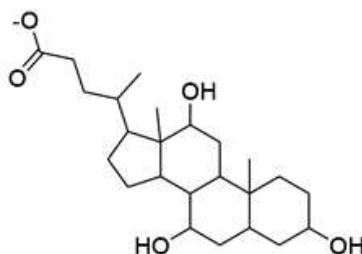
$X^- =$



(picrate)



(dodecylbenzenesulfonate)



(cholate)

12a, $n = 16$, $X^- = \text{PF}_6^-$: Cr 104 Cr' 126 SmA 138 Iso

12b, $n = 18$, $X^- = \text{PF}_6^-$: Cr 107 Cr' 126 SmA 176 Iso

12c, $n = 12$, $X^- = [\text{CuCl}_4]^{2-}$: Cr 54 Col_h 76 Iso

Importantly, these salts (**12**) exhibit a SmA phase with relatively large mesophase ranges that become relatively independent of the chain length for alkyl chain length greater than 14 carbon atoms. On the contrary, for the tetrachlorometalate(II) salts, the mesophase stability increases monotonically with an increase in chain length. While initially, the n-dodecyl derivative has been found to show only a SmA phase, later it was reported that this compound showed cubic and smectic A phases on the heating run, and columnar (16–46°C), cubic (46–66°C), and smectic A (46–143°C) phases on the cooling run. The authors found that the phase transition temperatures were strongly influenced by a glass surface and on the thermal history [15].

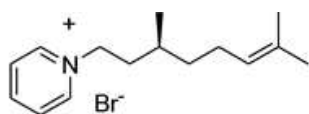
Replacement of chloride anion with bulkier hexafluorophosphate anion led to mesophase destabilization for pyridinium salts with alkyl chain shorter than 16 carbon atoms. Extensive studies were performed for N-alkyl pyridinium salts with alkylsulfates as counterion, all of them displaying a typical SmA phase, the mesophase temperature range depending on the combination of chain lengths of both N-alkyl and the aliphatic chain connected to the sulfate group [16, 17].

The tetrachlorocuprate pyridinium salts show a very interesting and rich polymorphism for alkyl chain longer than or equal to 12 carbon atoms, with hexagonal columnar, cubic, and SmA phases appearing in the order of increasing the chain length and/or temperature [18].

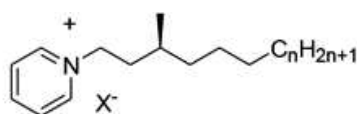
By exchanging the chloride anion with biologically active picrate, dodecylbenzenesulfonate, or cholate anions, different thermal behavior was found [19]. Thus, only the compound with dodecylbenzenesulfonate anion displayed a SmA phase stable up to 152°C, while the other two showed no liquid crystalline properties. The absence of mesomorphic properties in the case of picrate anion was attributed to the formation of interlayer 3-D hydrogen bond network between pyridinium and picrate ions.

2.2.3. Chiral *N*-alkylated pyridinium salts

Recently, a series of *N*-alkylated pyridinium salts containing a chiral center in the four positions with respect to nitrogen atoms have been prepared and investigated by Laschat et al. [20, 21]. Their thermal properties were compared to their imidazolium counterparts. Generally, these salts show a SmA phase, with melting and isotropization temperatures lower than the temperatures of their corresponding imidazolium counterparts. The mesophase stability range depends on the alkyl group length as well as on the counterion and it was found to decrease in the following order: $\text{Br}^- > \text{OAc}^- > \text{BF}_4^- > \text{I}^- > \text{SCN}^-$. The pyridinium salts with hexafluorophosphate anion show no liquid crystalline properties.



14



$\text{X}^- = \text{Br}^-, \text{I}^-, \text{SCN}^-, \text{BF}_4^-, \text{PF}_6^-, \text{OAc}^-$
 $n = 6-9$

15

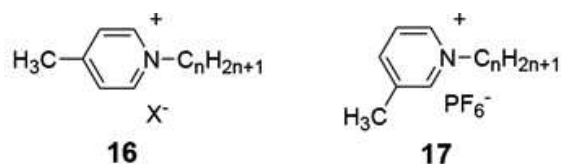
15a , $n = 9$, $\text{X}^- = \text{Br}^-$: Cr -8 Cr' -1 SmA 173 Iso	15d , $n = 9$, $\text{X}^- = \text{BF}_4^-$: Cr -19 Cr' 1 SmA 140 Iso
15b , $n = 9$, $\text{X}^- = \text{I}^-$: Cr -6 Cr' 41 SmA 171 Iso	15e , $n = 9$, $\text{X}^- = \text{PF}_6^-$: Cr 63 Cr' 80 Cr'' 126 Iso
15c , $n = 9$, $\text{X}^- = \text{SCN}^-$: Cr 2 Cr' 21 SmA 135 Iso	15f , $n = 9$, $\text{X}^- = \text{OAc}^-$: Cr 0 SmA 162 Iso

For chiral 1-citronellylpyridinium bromide salt **14**, only a glass transition was detected and no mesomorphism was evidenced.

2.2.4. *N*-alkylated pyridinium salts derived from picoline

The pyridinium salts derived from either 4- or 3-picoline, **16** and **17**, have been extensively studied [12, 22–24]. Their mesophase stability (SmA phase) depends strongly on the alkyl chain length as well as on the position of methyl group on the pyridinium ring. The mesophase temperature range increases significantly with increasing the alkyl chain length, while the alkyl substitution at the 3- and 4-positions on the pyridinium ring leads to a decrease in the melting point compared with the corresponding unsubstituted pyridinium salts. The effect of pyridinium ring substitution was also seen on the mesophase broadness, the pyridinium salts derived from 4-picoline having a much broader mesomorphic range compared to those derived from 3-picoline. Regarding the internal mesophase structure, the molecules are

considered to pack in an interdigitated fashion, with the anions sandwiched between the pyridinium rings.



$X^- = Br^-, I^-$
 $n = 12, 14, 16, 18, 20, 22$

$n = 12, 14, 16, 18$

$X^- = PF_6^-$
 $n = 12, 14, 16, 18$

16a, $n = 18$, $X^- = Br^-$: Cr 92 SmA 158 Iso

16b, $n = 20$, $X^- = Br^-$, Cr 84 SmA 197 Iso

16c, $n = 22$, $X^- = Br^-$, Cr 91 SmA 207 Iso

16d, $n = 22$, $X^- = I^-$: Cr 99 SmA 198 Iso

17a, $n = 12$, $X^- = PF_6^-$: Cr 56 Iso

17b, $n = 14$, $X^- = PF_6^-$: Cr 71 Iso

17c, $n = 16$, $X^- = PF_6^-$: Cr 75 Iso 60 SmA 55 Cr

17d, $n = 18$, $X^- = PF_6^-$: Cr 88 Iso 84 SmA 77 Cr

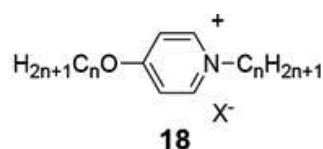
16e, $n = 12$, $X^- = PF_6^-$: Cr 55 Iso

16f, $n = 14$, $X^- = PF_6^-$: Cr 68 Iso

16g, $n = 16$, $X^- = PF_6^-$: Cr 74 Iso 61 SmA 58 Cr

16h, $n = 18$, $X^- = PF_6^-$: Cr 87 SmA 94 Iso

A series of N-alkylated pyridinium salts, having an alkoxy group in 4-position of pyridinium ring, were synthesized by the reaction of either N-alkyl-4-pyridones or 4-alkoxypyridines with corresponding alkyl bromides. Further, hexafluorophosphate and tetrafluoroborate pyridinium salts could be prepared by a metathesis reaction with the ammonium salts.



$n = 10, 12, 14, 16, 18$

$X^- = Br^-, PF_6^-, BF_4^-$

18a, $n = 12$, $X^- = Br^-$: Cr 70 SmA 120 Iso

18b, $n = 12$, $X^- = PF_6^-$: Cr 72 Iso 53 SmA 17 Cr

18c, $n = 12$, $X^- = BF_4^-$: Cr 39 SmA 77 Iso

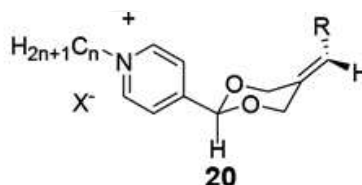
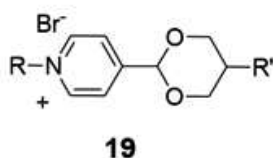
18d, $n = 14$, $X^- = Br^-$: Cr 77 SmA 140 Iso

18e, $n = 14$, $X^- = PF_6^-$: Cr 67 SmA 94 Iso

18f, $n = 14$, $X^- = BF_4^-$: Cr 51 SmA 98 Iso

These salts exhibit smectic A phase. The transition temperatures, both melting and clearing, as well as the mesophase stability were influenced by the alkyl chain length and the counterion type. The hexafluorophosphate anion, PF_6^- , produced smaller mesophase ranges, followed by tetrafluoroborate anion, BF_4^- , when compared to bromide pyridinium salts as a consequence of a weaker cation-anion interaction for the BF_4^- or PF_6^- than for the Br^- [5].

Pyridinium salts with a 1,3-dioxane ring attached in 4-position were prepared and their liquid crystalline properties were investigated [25, 26]. A very wide range for the SmA mesophase (between -24 and 150°C) was found for ionic thermotropic liquid crystal system having two rings in its central core (**19**) reported by Haramoto et al. [25]. Based on the same design, chiral pyridinium liquid crystals **20** show an interesting thermal behavior [26].



R = $\text{C}_{10}\text{H}_{21}$, $\text{CH}_2=\text{CH}-(\text{CH}_2)_8-$
 R' = C_2H_5 , $\text{CH}_2=\text{CH}-\text{CH}_2-$

n = 3, 10

X⁻ = Br⁻, I⁻, BF₄⁻, PF₆⁻, N(Tf)₂⁻

R = Br, Ph, p-MeO-C₆H₄, p-BuO-C₆H₄, p-OctO-C₆H₄, C₈H₁₇, C₁₈H₃₇

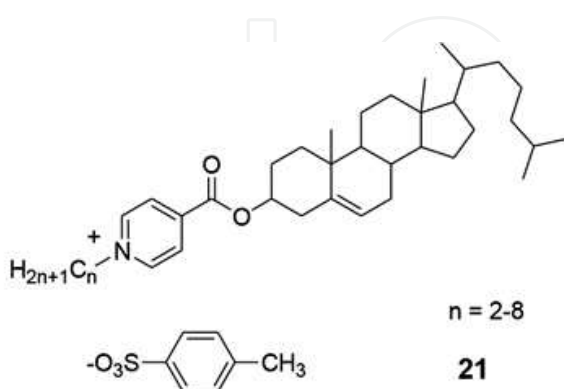
19a, Cr -24 SmA 150 Iso (R = $\text{C}_{10}\text{H}_{21}$, R' = C_2H_5)

20a, n = 10, R = C₁₈H₃₇, X⁻ = I⁻: SmX 41 N 90 Iso (dec.)

20b, n = 10, R = p-BuO-C₆H₄, X⁻ = I⁻: N 47 Iso

20c, n = 10, R = C₈H₁₇, X⁻ = Br⁻: SmC 53 Iso

First, LC phases were observed only for long alkyl chains on both sides of the molecule. Furthermore, the authors found that the enantiomeric purity influences significantly the nature of the mesophase (chiral nematic phase N* for pure single enantiomeric compounds and nematic and smectic phases for racemic mixture) and only slightly the transition temperatures between solid state and LC phase and LC phase and isotropic state. Moreover, the LC phase stability depends on the counterion size (higher stability for halide and tetrafluoroborate anions) due to the contribution of bigger anions to decreasing the packing of the mesomorphic cationic units. Yousif et al. found an enantiotropic cholesteric phase (N*) for a series of quaternized cholesteryl isonicotinates with tosylate counterions [27]. The assignment of such



n = 2-8

21a, n = 2, Cr 225 N* 241 Iso

21b, n = 3, Cr 176 N* 228 Iso

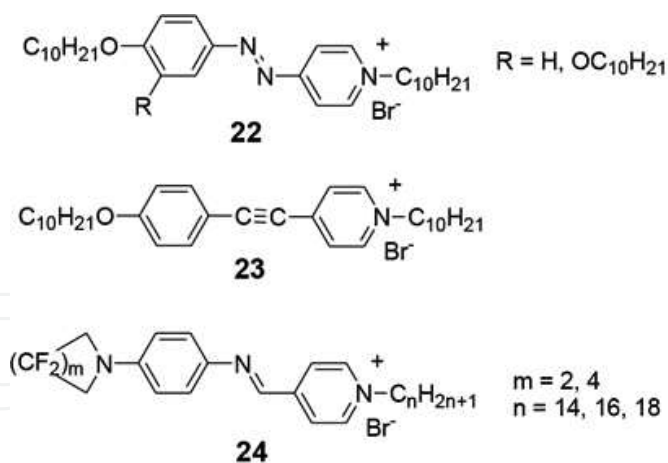
21c, n = 4, Cr 194 N* 225 Iso

21d, n = 5, Cr 181 N* 219 Iso

21e, n = 6, Cr 183 N* 236 Iso

21f, n = 7, Cr 177 N* 237 Iso

21g, n = 8, Cr 149 N* 218 Iso



- 22a**, $R = \text{H}$, Cr 119 SmA 138 Iso
22b, $R = \text{C}_{10}\text{H}_{21}$, Cr 86 SmA 119 Iso
23, Cr 174 SmA 183 dec
24a, $m = 2$, $n = 14$, Cr 87 M 156 Iso (dec.)
24b, $m = 2$, $n = 16$, Cr 90 M 159 SmA 175 Iso (dec.)
24c, $m = 4$, $n = 14$, Cr 80 Iso
24d, $m = 4$, $n = 16$, Cr 80 Iso

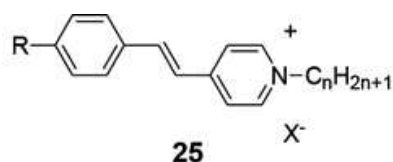
a mesophase was made based on polarizing optical microscopy when a planar texture with bright oily streaks was identified for such compounds. No additional XRD studies were undertaken to characterize this phase.

Several other pyridinium ILCs having a second aromatic ring connected to the 4-position of the pyridinium ring via a linking group (azo, **22**, acetylene, **23**, or imine, **24**) were designed and investigated [28, 29]. Their thermal properties are influenced by the alkyl chain length, the nature of linking groups, while the dominant factor for **24** was the size of perfluorinated ring [29].

2.2.5. *N*-Alkyl-4'-substitution-stilbazolium halides

N-alkyl-stilbazolium ILC, having different groups at the 4'-position of the stilbazolium head unit, were investigated by several authors [23, 30, 31]. The 4'-substitution at the stilbazolium unit has a great influence on the LC properties. For instance, the compounds with NO_2 or CN groups and bromide as counterion show a relatively narrow temperature range of the LC phase [30]. By introduction of chloride anions, the LC phase stability increases and the compounds decompose before reaching the isotropic phase. The use of dialkylamino group at the 4'-position in the stilbazolium core led to a significant decrease of the temperature range of the mesophase. For compounds **25a-f**, the substituents at the 4'-position of stilbazolium core increase the stability of the SmA phase in the following order: $\text{OCH}_3 > \text{OH} > \text{H}$, meaning that the mesomorphic behavior is also influenced by dipolar interactions resulting from OH and OCH_3 groups [23]. All these salts show an increase of the SmA phase range with increasing the alkyl chain length. On the other hand, the stability of the SmA phase is influenced by the size

of the counterion; lower melting and clearing temperatures were seen for iodide compared to bromide stilbazolium salts.



$n = 5 - 10$

$R = \text{NO}_2, \text{CN}$

$X^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$

$n = 14, 16, 18$

$R = \text{N}(\text{CH}_3)_2$

$X^- = \text{Br}^-$

$n = 14, 16, 18, 20, 22$

$R = \text{OH}, \text{OCH}_3, \text{H}$

$X^- = \text{Br}^-, \text{I}^-$

25a, $R = \text{H}$, $n = 18$, $X^- = \text{Br}^-$: Cr 153 SmA 217 Iso (dec)

25b, $R = \text{H}$, $n = 18$, $X^- = \text{I}^-$: Cr 189 Iso

25c, $R = \text{OH}$, $n = 18$, $X^- = \text{Br}^-$: Cr 172 SmA 230 Iso (dec)

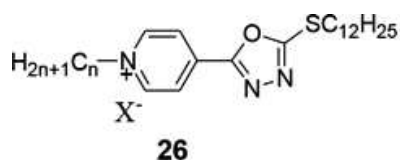
25d, $R = \text{OH}$, $n = 18$, $X^- = \text{I}^-$: Cr 130 SmA 184 Iso

25e, $R = \text{OCH}_3$, $n = 18$, $X^- = \text{Br}^-$: Cr 63 SmA 255 Iso (dec)

25f, $R = \text{OCH}_3$, $n = 18$, $X^- = \text{I}^-$: Cr 62 Cr' 245 Iso (dec)

2.2.6. Monocationic oxadiazole pyridinium salts

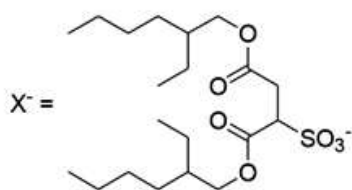
The pyridinium bromide salts **26a-d**, all of them show a SmA phase with a slight increase of clearing temperatures on increasing the alkyl chain length. By replacing the bromide ion with



$n=10,12,14,16$; $X^-=\text{Br}^-$

$n=12$

$X^- = \text{C}_m\text{H}_{2m+1}\text{SO}_3^-$
 $m=10, 14$



DOSS
bis(2-ethylhexyl)sulfosuccinate

26a, $n = 10$, $X^- = \text{Br}^-$: Cr 64 Cr' 117 SmA 172 Iso

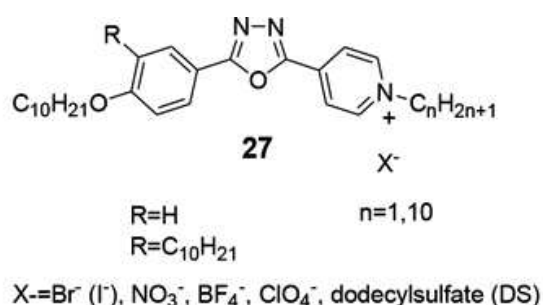
26b, $n = 12$, $X^- = \text{Br}^-$: Cr 74 Cr' 119 SmA 185 Iso

26c, $n = 14$, $X^- = \text{Br}^-$: Cr 70 Cr' 118 SmA 186 Iso

26d, $n = 16$, $X^- = \text{Br}^-$: Cr 85 Cr' 115 SmA 189 Iso

alkyl sulfate ions, a significant depression of clearing temperature was achieved (about 40°C) [32]. On the other hand, a total suppression of liquid crystalline phase was observed when the bis(2-ethylhexyl)-sulfosuccinate ion (DOSS) was employed. Interestingly, the pyridinium bromide salts display thermochromic properties [33]. Thus, the crystal to SmA transition of such compounds was accompanied with a color change from pale yellow to bright red that is almost fully reversible upon cooling. Such thermochromic effect was not observed on changing the bromide anion for alkylsulfate or DOSS ions. The origin of the thermochromic properties was attributed by authors to a charge-transfer couple formation between the bromide and the pyridinium ring.

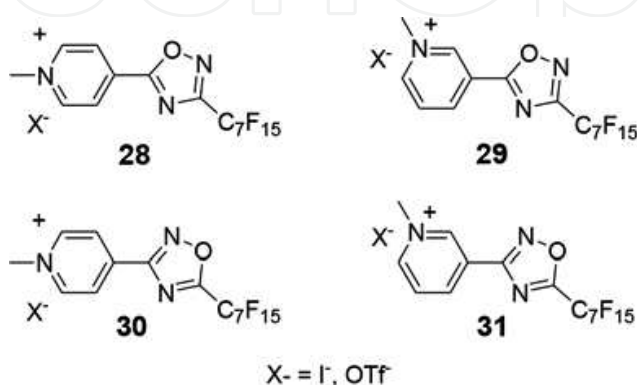
More recently, a systematic study of liquid crystalline and photophysical properties of a series of pyridinium salts was reported [34, 35], where the 1,3,4-oxadiazole unit connects one pyridinium ring and one mono- or di-substitution phenyl ring with alkoxy groups.



- 27a**, n = 1, R = H, X⁻ = BF₄⁻: Cr 193 SmA 256 dec
27b, n = 1, R = H, X⁻ = ClO₄⁻: Cr 202 SmA 257 dec
27c, n = 1, R = H, X⁻ = DS: Cr 122 SmA 208 dec
27d, n = 10, R = H, X⁻ = Br⁻: Cr 182 SmA 193 dec
27e, n = 10, R = H, X⁻ = NO₃⁻: Cr 126 SmA 171 dec
27f, n = 10, R = H, X⁻ = BF₄⁻: Cr 153 SmA 213 Iso
27g, n = 10, R = H, X⁻ = ClO₄⁻: Cr 167 SmA 217 Iso
27h, n = 10, R = H, X⁻ = DS: Cr 135 SmA 172 Iso
27i, n = 10, R = C₁₀H₂₁, X⁻ = Br⁻: Cr 148 SmA 194 dec

The N-decyl pyridinium salts exhibit SmA mesomorphism, regardless of the counterion, while their N-methyl counterparts show decomposition and no liquid crystalline properties for iodine and nitrate anions, and, for the remaining anions (BF₄⁻, ClO₄⁻, and DS), the salts decompose before reaching the isotropic phase from the previous SmA phase, suggesting that the thermal properties (melting point, mesophase range, and clearing or decomposition temperature) are sensitive to counterion exchange. Moreover, the two pyridinium salts with DS as counterion are similar in terms of thermal behavior, and this was explained by XRD studies. These compounds have a monolayered SmA phase, instead of a bilayered SmA phase found for the others compounds of the series, and the same molecular lengths (due to the presence of the same counterion), and such a different mesophase structure could account for their similar behavior.

An interesting example showing how the 3'- or 4'-substitution pattern of the pyridinium ring affects the thermal behavior is represented by the iodides and trifluoromethanesulfonates salts derived from perfluoroalkylated 1,2,4-oxadiazolylpyridines 28–31 [36]. Thus, the 3'-substitution derivatives exhibited liquid crystalline properties (SmX phase) on a narrow temperature range, while the corresponding 4'-substitution derivatives were found to pass from the crystalline state straight to the isotropic phase. Such a behavior was attributed to a charge delocalization over the entire structure, including the oxadiazole ring, which makes the cation/anion electrostatic interactions weaker and, thus, leading to the mesophase detabilization for 4'-substitution compounds.



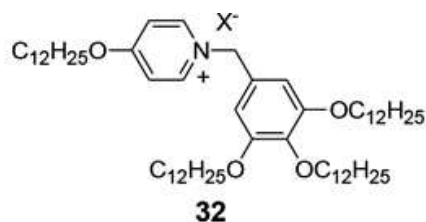
29a, X⁻ = I⁻: Cr 97 SmX 150 Iso

31a, X⁻ = I⁻: Cr 113 SmX 135 Iso

The fact that only the iodide salts showed liquid crystalline properties was explained by the greater coordinating ability of the iodide anions with respect to the trifluoromethanesulfonates anions. Moreover, all iodide salts showed thermochromism phenomena suggesting prospective applications in optoelectronics.

2.3. Monocationic pyridinium salts with mesogenic groups attached to nitrogen atom

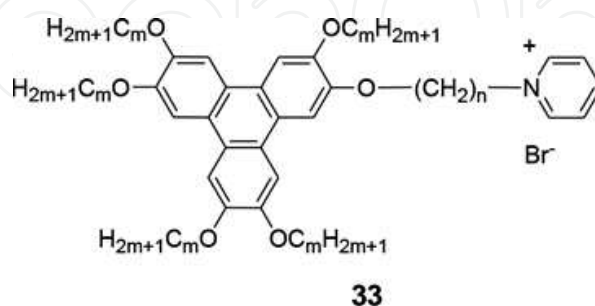
A series of pyridinium salts with the 3,4,5-tridodecyloxybenzyl moiety attached to nitrogen atom and different counterions (bromide, nitrate, tetrafluoroborate, and hexafluorophosphate) **32** were prepared starting from 4-hydroxypyridine [37].



X⁻ = Br⁻, NO₃⁻, BF₄⁻, PF₆⁻

32a, X⁻ = Br⁻: Cr 63 Col₁ 108 Iso 105 Col₁ 74 Col₂

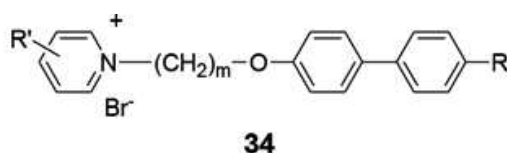
The pyridinium bromide salt shows one enantiotropic columnar mesophase and one additional monotropic columnar phase at lower temperatures. The size of counterion has a significant contribution to the LC phase stability. Surprisingly, when the bromide ion (Br^-) was replaced with bulkier counterions (NO_3^- , BF_4^- , and PF_6^-), the resulting products showed no liquid crystalline behavior. The photoluminescent properties of these pyridinium salts were investigated both in solution and solid state and it has been shown that their emission is only slightly influenced by the nature of counterion employed.



$$\begin{aligned} m &= 4, n = 5, 6, 7 \\ m &= 5, 6, n = 5 \end{aligned}$$

33a, $m = 4$, $n = 6$, Cr 84 Col 95 Iso

The classical triphenylene unit was connected to pyridinium ring via a flexible methylene flexible chain to give discotic liquid crystals [38]. The mesophase was identified to be a columnar phase based on microscopy observations of optical textures. The stability of this columnar phase was found to depend both on the peripheral alkyl chain length as well as the methylene spacer length. Thus, the stability of columnar phase increases by increasing the number of carbon atoms on the peripheral chains of the triphenylene core, while longer spacer connecting the triphenylene unit with the pyridine ring destabilized the mesophase.



$$\begin{aligned} m &= 6, 10 \\ R &= \text{CN}, -\text{OC}_n\text{H}_{2n+1}, n = 3, 10 \\ R' &= \text{H}, 4\text{-ethyl}, 2\text{-ethyl}, 3,5\text{-dimethyl} \end{aligned}$$

34a, $m = 6$, $n = 3$, $R' = \text{H}$, Cr 151 SmA 159 Iso

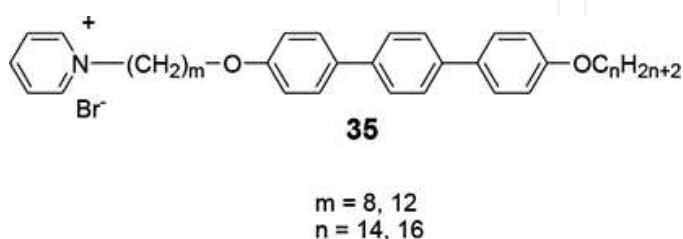
34b, $m = 10$, $n = 10$, $R' = \text{H}$, Cr 136 SmC 165 Iso

34c, $m = 10$, $n = 10$, $R' = 2\text{-ethyl}$, Cr 75 SmC 116 SmA 180 Iso

Interesting results were obtained for pyridinium bromides salts containing a biphenyl core and alkyl chains of different lengths **34** [39]. The substitution of the pyridine ring greatly influences the thermal behavior of these salts. While the unsubstituted pyridinium groups promote

mesomorphism (SmA and SmC phases), the 2- and 4-ethyl-substitution pyridinium groups give rise to liquid crystalline phases only with sufficiently long alkyl chains (decyl chains on both sides of the biphenyl core). The salts having a 3,5-dimethyl substitution pyridine ring do not show any liquid crystalline properties. Moreover, the substitution pattern at the pyridinium groups resulted in different types of smectic phases (SmA, SmC, and SmE).

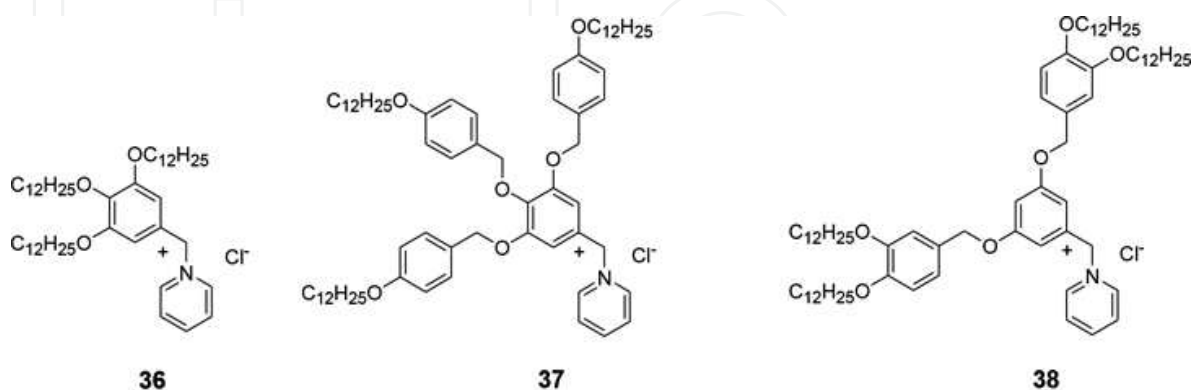
When an additional ring was added, the new pyridinium bromide salts **35** with a triphenylene moiety displayed tilted smectic mesophases (SmC) with molecules stacked in a double layer morphology, as indicated by XRD studies [40]. The tilt angle of these compounds shows a great temperature dependence, and, in fact, at lower temperature being closed to 0°.



The XRD studies together with molecular modeling indicated that π - π interactions counter-balance the strong ionic forces leading to a full segregation of molecular parts in the smectic structures.

2.3.1. Dendritic pyridinium ionic liquid crystals

Pyridinium chloride salts having dendritic building blocks connected to the nitrogen atom have been investigated by Percec et al. [41]. Depending on the number of peripheral alkoxy groups, these molecules were found to form columns or spheres, leading to 2D hexagonal columnar phases or a 3D cubic phase, respectively.



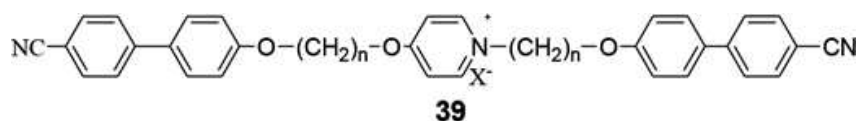
36, Cr 65 Col_h 166 Iso

37, Cr 15 Cr' 35 Cr'' 57 Col_h 159 Iso

38, Cr 17 Cr' 92 Col_h 129 Cub 164 Iso

2.3.2. Nematic pyridinium ionic liquid crystals

Starting from 4-hydroxypyridine, it is possible to attach two cyanobiphenyl mesogenic units, via flexible alkyl spacer, on both sides of the pyridinium ring giving rise to a series of nematic pyridinium liquid crystals [42]. The nematic phase has numerous technological applications due to its highest fluidity of all LC phases and hence the possibility to align it by applying an external electric/magnetic field. Moreover, the nematic phase is commonly used in electro-optical devices. The nematic phase is quite rare in the case of ILCs, several examples have been reported so far for ammonium [43, 44], imidazolium [45–48], pyridinium-based ILC [49], or miscellaneous type of ILC [50–54]. Generally, as the smectic phases are the most common phases for ILCs, especially due to electrostatic interactions, the nematic phase can be seen rather as an exception. It has to be reminded here the cholesteryl-containing compounds 21a–g that display a cholesteric phase (chiral nematic phase N*) at relatively high temperatures and on a narrow temperature range. Compounds **39**, all of them with the exception of **39d** and **39e**, displayed a monotropic nematic phase on cooling from the isotropic state. This is the first example of a series of ILC that exhibit a long range nematic phase, no matter the counterion or spacer length between the ionic core and the mesogenic group.



$n = 6, 9, 10$

$X^- = Br^-, NO_3^-, BF_4^-, PF_6^-, OTf^-, SCN^-$

- 39a**, $n = 6$, $X^- = Br^-$: Cr 120 Cr'144 Iso 70 N 23 g
39b, $n = 6$, $X^- = NO_3^-$: Cr 81 Iso 65 N 22 g
39c, $n = 6$, $X^- = BF_4^-$: Cr 57 Cr'85 Cr''102 Iso 60b N 24 g
39d, $n = 6$, $X^- = PF_6^-$: Cr 119 Iso 21 g
39e, $n = 6$, $X^- = OTf^-$: Cr 62 Cr'89 Iso 23 g
39f, $n = 6$, $X^- = SCN^-$: Cr 121 Iso 70 N 24 g
39g, $n = 9$, $X^- = Br^-$: Cr 128 Iso 89 N 28 g
39h, $n = 9$, $X^- = NO_3^-$: Cr 92 Cr' 103 Iso 92 N 26 g
39i, $n = 9$, $X^- = BF_4^-$: Cr 84 Cr'97 Iso 76 N 22 g
39j, $n = 9$, $X^- = PF_6^-$: Cr 114 Iso 41 N 21 g
39k, $n = 9$, $X^- = OTf^-$: Cr 104 Iso 45 N 20 g
39l, $n = 9$, $X^- = SCN^-$: Cr 92 Cr'110 Iso 89 N 21 g
39m, $n = 10$, $X^- = Br^-$: Cr 114 Iso 83 N 47 Cr
39n, $n = 10$, $X^- = NO_3^-$: Cr 99 Iso 86 N 25 g
39o, $n = 10$, $X^- = BF_4^-$: Cr 91 Iso 68 N 20 g
39p, $n = 10$, $X^- = PF_6^-$: Cr 120 Iso 40 N 21 g
39r, $n = 10$, $X^- = OTf^-$: Cr 72 Iso 44 N 10 g
39s, $n = 10$, $X^- = SCN^-$: Cr 95 Iso 82 N 40 Cr

The nematic phase was identified by using the combination of the three techniques: POM, DSC, and XRD, as well as, miscibility studies with 5 CB and doping with a chiral compound. A

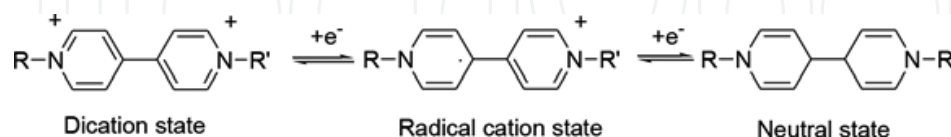
marbled texture or thread-like texture could be seen by POM, which flashed brightly under pressure, while several samples also exhibited regions with not well developed Schlieren texture. Previous examples of pyridinium ILC showing a Schlieren texture were assigned to a SmC phase [39]. For this reason, additional XRD studies were undertaken to rule out the possibility of misinterpretation of experimental data. Indeed, the diffractograms showed no sharp peaks in the low-angle region, but just a broad signal centered at 4.5 Å assigned to the average intermolecular separation, close to the typical value for liquid crystalline phases, confirming the nematic phase nature. Additional confirmation came from miscibility studies with common nematic LC, a mixture of **39i** 40% wt. and 5 CB displayed the N-Iso transition at 54°C. Furthermore, doping **39i** with a chiral dopant, a typical fingerprint texture could be seen by POM, a good indication of nematic phase. It has been shown that the temperature range of the liquid crystalline phase is greatly influenced by the spacer length and the nature of counterion employed. In fact, the very bulky PF₆[−] and OTf[−] anions have a great contribution to the destabilization of nematic phase.

The NMR data are strongly dependent on the anion-cation interaction specific to ILC, and they can be related to the presence of hydrogen-bonding interactions that cause downfield chemical shift of the related H atoms for imidazolium- and pyridinium-based ILC. Stronger interactions with anions lead to further downfield chemical shifts, in particular for C-H adjacent to nitrogen atom. The chemical shifts of these protons, from the ¹H NMR spectra of pyridinium salts **39a-s**, were found to follow the order: Br[−] > SCN[−] ~ NO₃[−] > OTf[−] > BF₄[−] > PF₆[−].

3. Dicationic bis(pyridinium) and polycationic pyridinium salts

3.1. 4,4'-Bipyridinium-based ionic liquid crystals

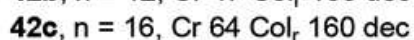
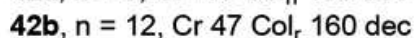
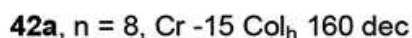
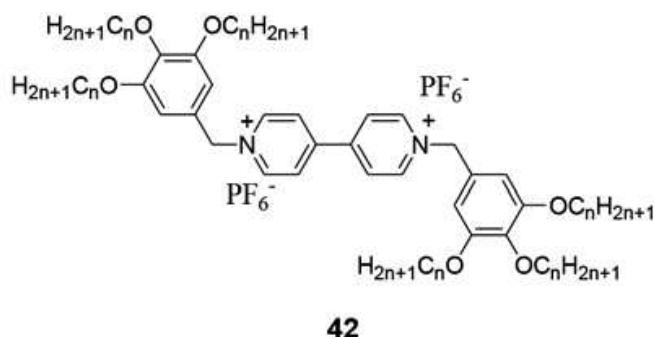
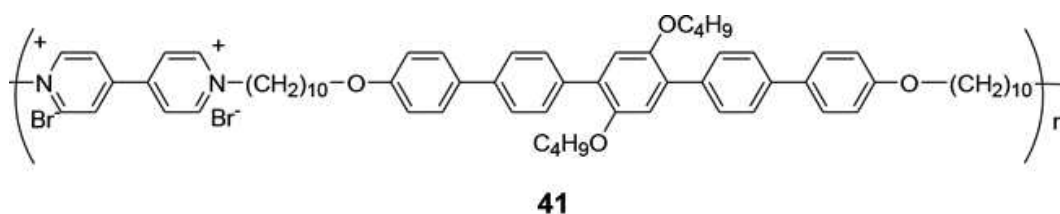
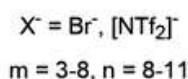
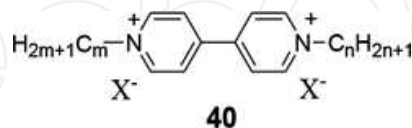
The 4,4'-bipyridinium salts or viologens are a special class of materials that show interesting properties, such as electrochromism and electrical conductivity, which were successfully employed in producing liquid crystalline materials. The reports dealing with liquid crystals based on 4,4'-bipyridinium salts significantly grew after 2000. It is important to mention that such materials can be part of a two steps reduction process, and this process is reversible, as depicted below.



Additionally, it is of interest to note here that many dicationic and tetracationic ILC based on the 4,4'-bipyridinium rigid core (viologen-based ILC) have been investigated so far, displaying mesomorphic properties typically of calamitic and discotic materials [55–59].

The mesogenic properties of compounds based on asymmetric viologen salts of bis(trifluoromethanesulfonyl)amide ([NTf₂][−]) **40** were influenced by their symmetry. It was found that the strongly asymmetric system does not display mesomorphic behavior, having low melting points (below 40°C). The less asymmetric products exhibit a smectic phase (SmB) with a wide

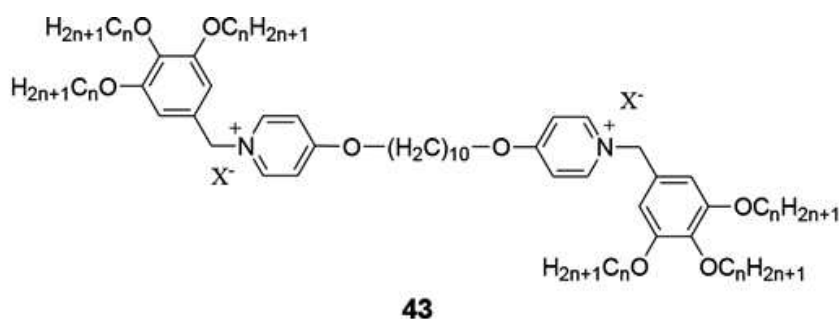
range of stability, from about 0°C up to above 140°C. More structural changes on these 4,4'-bipyridinium systems, in general, give rise to more ordered smectic phases. 4,4'-bipyridine group can also be employed to prepare polymeric liquid crystals **41**, and one example bearing a pentaphenylene connecting group via flexible chain length is presented below [60]. This polymeric ionic liquid crystal shows single layer smectic-type mesophases, both tilted (SmC) and orthogonal (SmA) phases.



Columnar phases could be obtained for liquid crystals bearing two 3,4,5-tris(alkoxy) benzyl units attached to the 4,4'-bipyridinium moiety [61]. The viologen product bearing six octyloxy chains shows a hexagonal columnar (Col_h) phase, while the analogues with longer alkoxy chains (12 or 16) show rectangular columnar (Col_r) phases. For these products, the clearing temperatures could not be measured due to thermal degradation before reaching the isotropic state. Different molecular packing (Col_h or Col_r) was explained by formation of more elliptical molecular structures for compounds with elongated terminal alkoxy chains that may prefer to form the Col_r phases.

3.2. Dicationic bis(pyridinium) salts with flexible linker

Bis(pyridinium) salts with flexible spacers **43** derived from 4-hydroxypyridine containing mesogenic 3,4,5-tris(alkyloxy)benzyl moieties (alkyl = dodecyl or tetradecyl) on each side and various counterions, such as bromide (Br^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), and triflate (OTf^-), were reported recently [62]. While there are numerous examples of dicationic pyridinium ILC, this one represents the first example of this type. These dicationic pyridinium salts display an enantiotropic liquid crystalline behavior with a hexagonal columnar (Col_h) phase assigned on the basis of their characteristic texture, pseudo-focal conic and spherulitic textures, when observed by POM and XRD studies. The temperature range of the hexagonal columnar phase is greatly influenced by the terminal chain length (12 or 14) and the nature of counterion employed. For example, the triflate salt with 12 carbon atoms in the terminal chains, **43d**, has the lowest melting point, 15°C , below ambient temperature and does not show any mesogenic behavior. It was found that the thermal behavior resembles the general trend found for pyridinium ILC, where transition temperatures show a decreasing tendency with an increase in the size of anions. Furthermore, the compounds with higher number of carbon atoms have higher melting points and isotropization temperatures with broader mesophase ranges (31°C for **43a** and 40°C for **43e**).



$n = 12, 14$

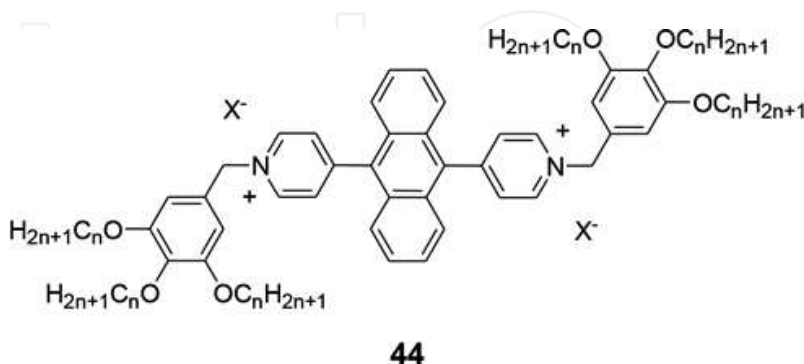
$X^- = \text{Br}^-, \text{PF}_6^-, \text{BF}_4^-, \text{OTf}^-$

43a , $n = 12$, $X^- = \text{Br}^-$: Cr 21 Cr' 39 Col_h 70 Iso	43e , $n = 14$, $X^- = \text{Br}^-$: Cr 39 Col_h 79 Iso
43b , $n = 12$, $X^- = \text{PF}_6^-$: g 8 Col_h 87 Iso	43f , $n = 14$, $X^- = \text{PF}_6^-$: Cr 34 Col_h 100 Iso
43c , $n = 12$, $X^- = \text{BF}_4^-$: Cr 14 Col_h 84 Iso	43g , $n = 14$, $X^- = \text{BF}_4^-$: Cr 37 Col_h 77 Iso
43d , $n = 12$, $X^- = \text{OTf}^-$: Cr 15 Iso	43h , $n = 14$, $X^- = \text{OTf}^-$: Cr 36 Col_h 47 Iso

The study of emission properties of these luminescent bis(pyridinium) salts revealed a weak emission in dichloromethane solutions at room temperature, with quantum yields up to 4.4%. Their solid-state emission is significantly red shifted by comparison to solution emission spectra recorded in dichloromethane, suggesting a more complex emission mechanism, probably an aggregate-type emission in solid state [62].

3.3. Dicationic bis(pyridinium) salts with a rigid core

Dicationic pyridinium salts with an anthracene moiety connecting two pyridine rings substitution with tris(alkoxy)benzyl groups **44** were designed and investigated for their liquid crystalline properties and stimulus responsive luminescence [63].



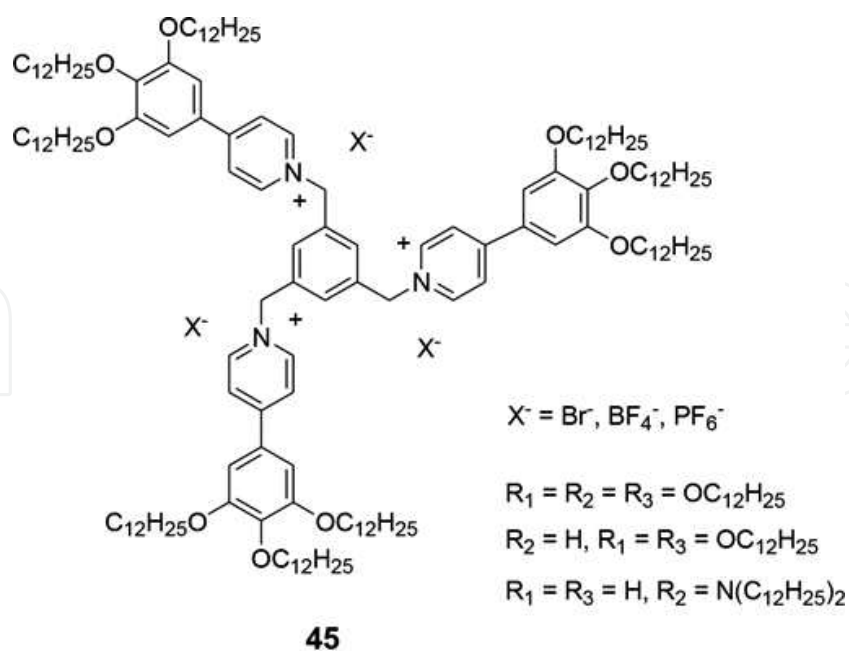
$n = 8, 12$
 $X^- = Br^-, BF_4^-, PF_6^-$

44a, $n = 8$, $X^- = Br^-$: Cr 197 Col_r 228 dec **44d**, $n = 12$, $X^- = Br^-$: Cr 203 Col_r 235 dec
44b, $n = 8$, $X^- = PF_6^-$: Cr 216 Iso 151 Col_r **44e**, $n = 12$, $X^- = PF_6^-$: Cr 220 Iso 148 Col_r
44c, $n = 8$, $X^- = BF_4^-$: Cr 181 Col_r 218 dec **44f**, $n = 12$, $X^- = BF_4^-$: Cr 185 Col_r 205 dec

The anthracene moiety act as a fluorophore in the center of molecules, and the solvate of pyridinium salts **44**, $n = 1$, show piezoluminescence by grinding. The anion has an influence on the LC phase stability and thus, the long alkyl chain derivatives **44a-f** show either enantiotropic (for bromide and tetrafluoroborate salts) or monotropic (in the case of hexafluorophosphate salts) rectangular columnar phases.

3.4. Tripodal pyridinium ILC

Photoluminescent tripodal pyridinium-based ionic liquid crystals were reported by Kato et al. [64, 65]. These tricationic pyridinium salts show thermotropic hexagonal or rectangular columnar phases or cubic phases with a large temperature ranges. The columnar or cubic phase stability is given by the difference in the anion size. For small-size anions (bromide), the cationic pyridinium cores should be packed more closely through electrostatic interactions and hence, the molecules prefer to self-assemble in cubic structures at higher temperatures (**45a**). Upon photoirradiation with UV light, these pyridinium salts emit blue-green or green light with photoluminescence quantum yields rather low, 3–6% in solution [65].



45a, $X^- = \text{Br}^-$: Cr 77 Col_h 179 Cub 245 Iso

45b, $X^- = \text{BF}_4^-$: Cr -3 Col_h 160 Iso

45c, $X^- = \text{PF}_6^-$: Cr 13 Cr' 24 Col_r 245 Iso

Acknowledgements

This work was supported by a grant of the Romanian Authority for Scientific Research, CNCS-UEFISCDI, and project number PN-II-ID-PCE-2011-3-0384.

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